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FACTORS AFFECTING PROPERTIES OF SOL-GEL FILMS

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A relationship between the refractive index, the mirror reflection factor, the Vickers microhardness, and the chemical resistance of sol-gel films and the film thickness, inclination to crystallization, structural specifics, and composition is established.

The interest in new types of glass, known as "cold windows," i.e., materials capable of reflecting sunlight, weakening the heat flow penetrating from outside and overheating the interior spaces calls for research in this direction.

The most economical and, consequently, the most promising method for producing such materials is modification of the surface of standard sheet glass using thin sol-gel films, i.e., solid coatings.

The principal stages of the sol-gel technology are generally known [1]. The main problems confronted by developers of solid coatings are selection of a highly reflective composition and producing film of a required thickness, which would allow for efficient reflection of light and heat flows in a prescribed range of the spectrum.

In accordance with the widespread concept of sol-gel film as a thin layer of glass deposited on a substrate [1], it would appear that the development of a composition for coating should not be difficult: the reflection factor of a material is directly proportional to its refractive index [2], and the refractive index of glass is an additive property which can be calculated with a high degree of accuracy using the methods by A. A. Appen or L. I. Demkina [3, 4]. However, practice has shown that frequently the measured values of this property differ significantly from the expected values, and equimolecular substitution of certain oxides in a film composition for other oxides produces unexpected results. This calls for labor-intensive research to identify the relationship of the composition to the properties of thin sol-gel films in each specific case.

The purpose of the present study is to determine and clarify the factors which, along with the composition, affect certain physical and physicochemical properties of solid coatings.

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For our research we selected a number of presumably highly refractive compositions, which contained two or three oxides each from those listed below:

Oxide	Refractive index [4]
Titanium (IV)	2.13
Silicon (IV)	1.475
Bismuth (III)	2.45
Lanthanum (III)	2.08
Antimony (III)	2.07
Indium (III)	2.01
Iron (III)	2.01

* According to data in [5].

The methods for preparing film-forming solutions (FFS), their deposition, monitoring of properties, and firing of coatings are described in detail in [6, 7]. Note that the total weight content of oxides in the solutions varied from 2.5 to 5%, the rate of application of solution on glass remained constant (1 m/sec), and the samples were heat-treated at 450°C for 30 min.

Table 1 presents the molar content of oxides (by synthesis) in 11 studied films; the total weight content of oxides in FFS; refractive index values (estimated according to the method in [4]) of glasses whose composition is identical to that of film coatings; confidence intervals of distribution of the refractive index measured values; mirror reflection coefficient; Vickers microhardness; chemical resistance of samples with coatings; average thickness of films; oxide content in coatings (estimated) considering diffusion of components from the glass substrate. As can be seen, all measured properties depend to a large extent on the total weight content of oxides in the FFS.

The glass batch in glass melting is analogous to a film-forming solution. Glass produced by traditional melting of a

mixture of raw materials has low sensitivity to the moisture of this mixture. The refractive index of optical glass, even when it is made of a solution containing all the necessary oxides, does not differ from the catalog value, within the limits of experimental error [8]. This difference in the behavior of glass and sol-gel coating is due to a number of reasons, the main of them, in our opinion, being the fact that glass and film are not identical material with respect to their structure. The solid coating, most probably, is a material in which the glass-forming process is "frozen" at a certain intermediate stage, i.e., a solid body with a certain "vitreous index" is formed. It may be assumed that this index is below 1, since the temperature (significantly lower than the starting point of deformation of the glass substrate) and duration of heat treatment are not substantial. Moreover, unlike glass, the film is a porous material, which also introduces some corrections. As a consequence, the expected refractive index is always higher than the actually measured one.

As can be seen from Table 1, the estimated refractive indexes of the studied films vary from 2.15 (for coating composition 80% La_2O_3, 20% Bi_2O_3) to 1.95 (80% In_2O_3, 20% SiO_2) and the confidence intervals of distribution of the measured values of the refractive index are 1.535 – 1.528 and 1.684 – 1.596 for both specified films produced from a solution with a total weight content of oxides equal to 2.5%. Let us consider the reasons for this circumstance.

It is known that crystals emerging in glass modify its refractive index. However, the difference between the expected and the measured values of the refractive index is not always associated with heterogeneity of coating microstructure (Table 1 and Figs. 1 and 2). Apparently, one should take into account diffusion of the substrate components.

Let us compare the average measured value of the refractive index with the estimated value (taking into account modification of the composition due to the diffusion of the glass substrate components) for two iron-containing films (Table 1). For the coating with 80% In_2O_3, 20% SiO_2, and Fe_2O_3, the measured and the estimated values are close. For the film 80% La_2O_3, 20% Bi_2O_3, Fe_2O_3 the measured value is below the expected value, presumably due to the presence of inclusions (Fig. 3).

Therefore, the refractive index of the film is lower than the refractive index of the glass with the same composition for at least two reasons: the diffusion of poorly refractive components from the glass substrate, and the heterogeneous structure of the coating. Moreover, as distinct from glass whose crystallization level can often be controlled by the melting, molding, and annealing regime, it is virtually impossible to control the amount of inclusions in a film due to restrictions with respect to the regime of solution preparation, deposition, and heat treatment of solid coatings in sol-gel technology.

In this context it is easy to account for the dependence of the refractive index of film on the content of oxides in the solution. The higher the content, the thicker the coating and the more intense the crystallization, whereas the diffusion of poorly refractive components from the substrate to the film-air interface is, on the contrary, weaker. The first factor contributes to a decrease, and the second one to an increase in the refractive index level. It is hard to predict which of the specified processes will be predominant in each specific case.

As for the mirror reflection factor, it depends not only on the refractive index, but on the tendency of film to crystallization. Sometimes, the effect of the latter factor is so substantial that the reflection factor of a highly refractive coating due to light diffusion on inclusions is unexpectedly low (Table 1 and Figs.1 – 3).

Thus, the effect of a prescribed composition on the film properties is expressed indirectly through the diffusion of

TABLE 1

Molar content in film (by synthesis), %	Weight content of oxides in FFS, %	Estimated refractive index	Confidence intervals of measured values of				Film thickness, Å
			refractive index	mirror reflection factor, %	microhardness, MPa	chemical resistance, %*	
80 La_2O_3, 20 Bi_2O_3	2.5	2.154	1.535 – 1.528	10.0 – 9.0	6510 – 6238	31 – 18	312
80 La_2O_3, 20 Sb_2O_3	2.5	2.078	1.738 – 1.662	16.1 – 12.7	6563 – 6287	10 – 3	236
80 La_2O_3, 20 Bi_2O_3**	2.5	1.781	1.830 – 1.665	14.2 – 13.0	7000 – 6780	81 – 43	412
80 TiO_2, 20 La_2O_3	5.0	2.114	1.763 – 1.650	17.8 – 15.4	6458 – 6140	19 – 12	1282
80 TiO_2, 20 La_2O_3	2.5	2.114	1.819 – 1.734	23.9 – 17.5	6521 – 6303	22 – 2	418
80 Sb_2O_3, 20 La_2O_3	5.0	2.072	1.918 – 1.859	35.2 – 19.8	6257 – 6111	50 – 29	980
80 Sb_2O_3, 20 La_2O_3	2.5	2.072	1.871 – 1.797	30.4 – 18.9	6559 – 6517	43 – 25	345
80 In_2O_3, 20 Bi_2O_3	2.5	2.100	1.801 – 1.778	10.1 – 8.9	6486 – 6290	36 – 27	386
80 In_2O_3, 20 SiO_2	5.0	1.948	1.566 – 1.517	10.4 – 8.6	6659 – 6379	57 – 43	1288
80 In_2O_3, 20 SiO_2	2.5	1.948	1.684 – 1.596	14.6 – 11.2	6745 – 6413	17 – 8	375
80 In_2O_3, 20 SiO_2***	2.5	1.663	1.720 – 1.694	19.7 – 16.3	6690 – 6310	60 – 44	383

* Is characterized by a relative loss in the film thickness after holding of the sample in 0.1 N solution of HCl for 30 min.

** 20 wt.% Fe_2O_3 (above 100%) was introduced into the film. The molar content of film components, taking into account the substrate diffusion, amounted to (%): 35.6 La_2O_3, 9.1 Bi_2O_3, 19.6 Fe_2O_3, 12.2 Na_2O, 3.1 CaO, 20.4 SiO_2.

*** The same, 22.0 In_2O_3, 6.0 SiO_2, 8.0 Fe_2O_3, 16.0 Na_2O, 7.0 CaO, 41.0 SiO_2.

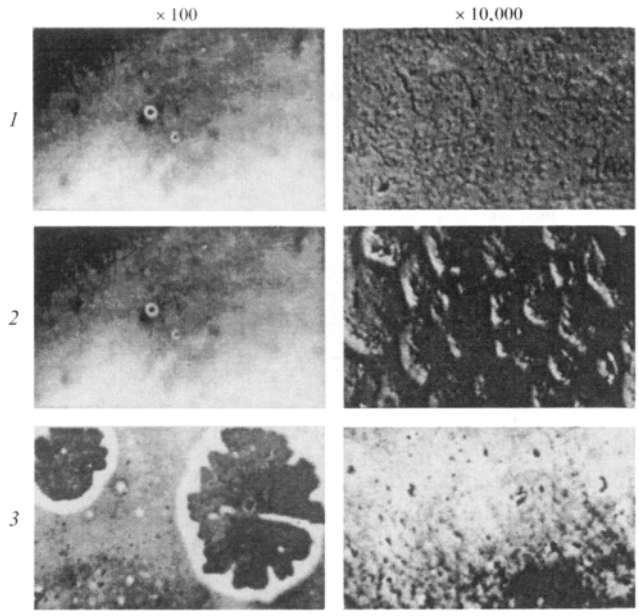

Fig. 1. Microphotos of sol-gel films obtained from solutions with total weight content of film-forming oxides equal to 5%. Molar content in the composition (%): *1*) 80 In_2O_3, 20 SiO_2; *2*) 80 TiO_2, 20 La_2O_3; *3*) 80 Sb_2O_3, 20 La_2O_3.

substrate components. Its intensity is closely related to the type and size of cations integrating the coating. After deposition of a FFS on glass, the film components presumably form a primary matrix which has certain packing density, porosity, and inclination to crystallization. The components migrating from the substrate penetrate into microcavities and in heat treatment presumably react to the coating components, as a consequence of which a secondary, more multicomponent composition is formed, as well as a microstructure responsible for the crystallization capacity and the properties of the thin film.

Since the inclusions and (or) crystals have a negative effect on the optical parameters of articles with sol-gel coatings, a logical question arises whether their emergence can be predicted. It follows from Figs. 1 and 2 that the film with 80% TiO_2 and 20% La_2O_3 is a crystallizing one. Crystallization is naturally weaker in a thinner film produced from the FFS with a lower overall content of oxides. According to data in [9], there is a chemical compound corresponding to formula $2La_2O_3 \cdot 9TiO_3$, whose composition is close to the specified film.

In the development of new glasses the following rule is observed: the maximum crystallizing capacity among the vitreous systems within the limits of the crystallization field of a particular compound is exhibited by the glass whose composition corresponds to the composition of the compound [4]. This rule can be applied to the development of sol-gel coatings as well. Any increase in the complexity of a glass composition decreases its crystallizing capacity [4]. Considering this, variations in the crystallizing capacity observed in films which have identical composition but different thickness can possibly be attributed to the different intensities of migration of the substrate components. As is known from practice, the amount of oxides penetrating into a thin film is 1.2 – 1.3 times higher than the amount of oxides migrating into a thick film of the same chemical composition.

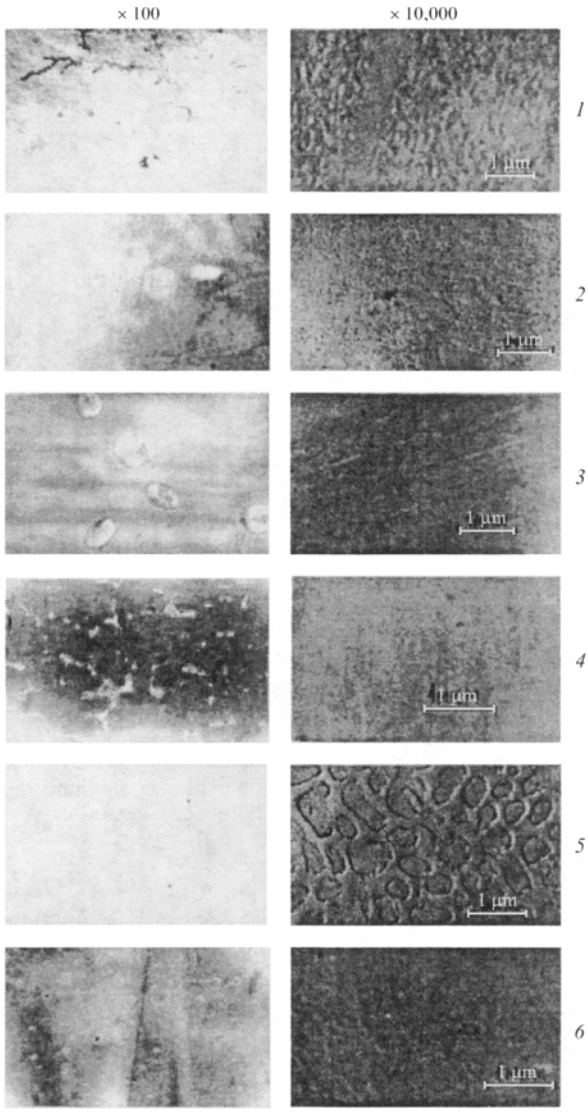

Fig. 2. Microphotos of sol-gel films obtained from solutions with total weight content of film-forming oxides equal to 2.5%. Molar content in the composition (%): *1*) 80 In_2O_3, 20 SiO_2; *2*) 80 In_2O_3, 20 Bi_2O_3; *3*) 80 La_2O_3, 20 Bi_2O_3; *4*) 80 La_2O_3, 20 Sb_2O_3; *5*) 80 TiO_2, 20 La_2O_3; *6*) 80 Sb_2O_3, 20 La_2O_3.

Thus, the composition of a coating formed on the glass surface after deposition and heat treatment differs significantly from the prescribed composition. Therefore, a reliable prediction of the properties of a glass article with a modifying film is possible only in the case where there are precise data on the extent of the effect of this film-forming composition on the substrate diffusion and the variations in the structure and phase composition which may be caused by this migration.

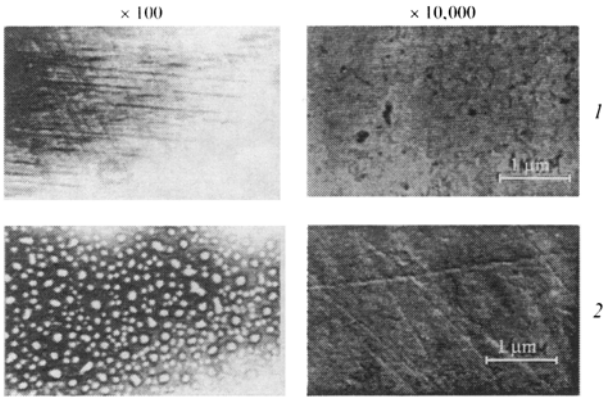

Fig. 3. Microphotos of sol-gel films obtained from solutions with total weight content of film-forming oxides equal to 2.5%. Molar content in the composition (%): *1*) 80 In_2O_3, 20 SiO_2; *2*) 80 La_2O_3, 20 Bi_2O_3; both films contain ferric oxide.

Consider the relationship between the microhardness and chemical stability of a modified article and the structure of the film.

The microhardness of the film with 80% In_2O_3 and 20% SiO_2 is slightly higher than that of the coating containing 80% TiO_2 and 20% La_2O_3; the first film regularly contains fine inclusions (less than 0.1 μm) and the second one contains large inclusions, up to 1.0 – 1.5 μm (Fig. 1 and Table 1).

The microhardness of the coating with 80% Sb_2O_3 and 20% La_2O_3 appears to be higher than that of films containing 80% La_2O_3, 20% Bi_2O_3 and 80% In_2O_3, 20% Bi_2O_3, due to structural differences similar to those described above (Fig. 2 and Table 1).

Finally, the data in Fig. 3 and Table 1 substantiate the validity of the rule presented in [10]: extended chain structures arising in a coating impart high microhardness to it. Apparently, not only the shape but the composition of inclusions as well have a role in this process. In any case, the film microhardness in the $Bi_2O_3 - Fe_2O_3 - TiO_2$ system, in which TiO_2 is assumed to be responsible for the formation of the mentioned inclusions, and in the $CuO - TiO_2$ system, in which the emergence of dendrite crystals is associated with the presence of $CuCl_2 \cdot 2H_2O$ [7], is different: 7086 – 6998 and 6845 – 6555 MPa, respectively [7, 10]. The microhardness of the film containing 80% La_2O_3, 20% BiO_3, Fe_2O_3 is equal to 7000 – 6780 MPa.

If the change in the coating thickness does not entail perceptible structural transformations, the microhardness virtually does not change. A decrease in the size of inclusions increases the microhardness of the film containing 80% Sb_2O_3, 20% La_2O_3 produced from a FFS with the total weight content of oxides equal to 2.5%.

Complication of the composition by adding ferric oxide affects the microhardness in the case where this additive entails significant changes in the structure, as, for example, in the film with 80% Bi_2O_3, 20% La_2O_3 after the introduction of Fe_2O_3.

The destruction of any material under the effect of aggressive medium depends on its composition and porosity. Pores facilitate the penetration of the etching agent in the depth of the body and intensify dissolution. The experience shows that in similar heat treatment the porosity of the film is proportional to its thickness. At the same time, the concentration of the components penetrating from the substrate into a thin film (including SiO_2 which increases chemical resistance) is higher than such concentration in a thick film. All this contributes to the improvement of the chemical resistance of coatings, As can be seen from Table 1, introduction of ferric oxide degrades chemical resistance. The ability of a coating to withstand the destructive effect of the etching agent probably depends as well on the type of oxides which are part of its composition. It can be suggested that if the composition contains oxides that are resistant to a particular aggressive medium, the film will be chemically resistant as well. This assumption is supported by an analysis of the results presented in Table 1. Replacement of Sb_2O_3 or Bi_2O by SiO_2 and TiO_2, which are virtually insoluble in hydrochloric acid, regularly improves the chemical resistance of the coatings. Complication of the composition using ferric oxide, which relatively easily dissolves in HCl [11], decreases chemical resistance.

Thus, the properties of sol-gel films of identical composition depend to a great extent on the film thickness. A decrease in the film thickness and introduction of oxides that are not soluble in hydrochloric acid increase the chemical resistance of the film.

REFERENCES

1. N. V. Suikovskaya, *Chemical Methods for Production of Thin Transparent Films* [in Russian], Khimiya, Leningrad (1971).
2. H. Kukhling, *Physics Reference Book* [in Russian], Mir, Moscow (1982).
3. A. A. Appen, *Chemistry of Glass* [in Russian], Khimiya, Leningrad (1972).
4. *Physicochemical Principles of Optical Glass Production* [in Russian], Khimiya, Leningrad (1976).
5. *Inorganic Compounds. Reference Book* [in Russian], Khimiya, Leningrad (1983).
6. A. B. Atkarskaya, V. I. Borul'ko, V. Yu. Goikhman, et al., "Interrelation of technological and qualitative parameters of thin-layer coatings," *Steklo Keram.* No. 6, 10 (1992).
7. A, B. Atkarskaya, V.i. Borul'ko, and V. I. Rastorguev, "Alkoxide sol-gel coating of TiO_2 – CuO system," *Tr. Inst. Ukrainian State Institute of Glass*, Issue 1, 39 – 50 (1994).
8. A. B. Atkarskaya, "Development of compositions and principles for production of glass for VOLS," *Author's Abstract of Candidate's Thesis* [in Russian], Leningrad (1984).
9. Ya. G. Goroshchenko, *Chemistry of Titanium* [in Russian], Naukova Dumka, Kiev (1970).
10. A. B. Atkarskaya, "Structural phase transformations and properties of thin films of $Bi_2O_3 - FeO_3 - TiO_2$ system," *Steklo Keram.* No. 11, 9 – 12 (1995).
11. B. V. Nekrasov, *Principles of General Chemistry* [in Russian], Vol. 3, Khimiya, Moscow (1970).